

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date
8 December 2005 (08.12.2005)

PCT

(10) International Publication Number
WO 2005/116761 A2

(51) International Patent Classification⁷:

G03F 7/00

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(30) Priority Data:

60/575,014

27 May 2004 (27.05.2004) US

(71) Applicant (for all designated States except US): E.I. DUPONT DE NEMOURS AND COMPANY [US/US]; 1007 MARKET STREET, WILMINGTON, Delaware 19898 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): KIM, Young, H. [US/US]; 406 Bartram Lane West, Hockessin, Delaware 19707 (US).

(74) Agent: LANGWORTHY, John, A.; E. I. DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

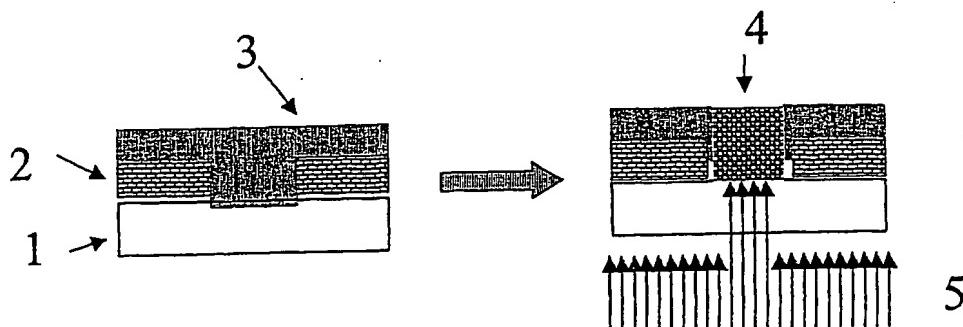
Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: UV RADIATION BLOCKING PROTECTIVE LAYERS COMPATIBLE WITH THICK FILM PASTES

WO 2005/116761 A2



(57) Abstract: This invention relates to compositions comprising a photoresist material and a UV-B blocking agent. These compositions are used in the fabrication of electronic devices, particularly those formed from thick film pastes. The present invention is also an electronic device fabrication process using the compositions. A protective polymer layer is fabricated from materials that are insoluble after irradiation in the ester-type solvents contained in a thick film paste. By appropriate selection of protective film polymers, the protective film can be used to photo-image a pattern with an unfiltered mercury lamp radiation source.

TITLEUV RADIATION BLOCKING PROTECTIVE LAYERS
COMPATIBLE WITH THICK FILM PASTES

5

This application claims the benefit of U.S. Provisional Application No. 60/575,014, filed May 27, 2004, which is incorporated in its entirety as a part hereof for all purposes.

10

Field of the Invention

The present invention relates to a composition and a process that involves the use of a protective layer in the fabrication of electronic devices from thick film pastes.

Technical Background

The present invention relates to a composition and a process for constructing electronic devices wherein a substrate is coated with a conducting layer that is in turn coated with a thick film paste. The thick film paste may contain materials such as glass frits, conductors, photo-imageable polymers, and, usually, a solvent.

In the fabrication of these devices, photo-imageable protective layers may be used to isolate photo-imageable thick film deposits from other elements of these electronic devices such as conductive layers. A problem arises in some of these devices in that the solvent used in a thick film paste, usually an ester or ether type solvent, is frequently damaging to the polymeric protective layer and may lead to "short circuits". This can lead to problems on the surface of the substrate such as peeling or dissolution of the

protective layer from the substrate when that layer is exposed to the thick film paste. It is desirable that the protective layer can be patterned to accommodate the inclusion of the thick film paste material at the 5 position desired. The use of unfiltered mercury lamps in the patterning process can expose the protective layer to UV-B radiation. UV-B radiation exposure can cause portions of the protective layer to become insoluble, which may leave an undesirable residue after 10 development.

Wang et al in the Proceedings of the SPIE - *The International Society for Optical Engineering* (1999) vol. 3906, p. 619-24 describe the electrical 15 characterization of polymer thick film resistors. Fukuda (US 5,601,638) describes a thick film paste for use in the formation of circuit components. Ezaki (US 5,362,927) reports a thick film hybrid circuit board device formed by lamination. Kazunori 20 (JP 2001/155,626) provides a method for producing a display substrate. Takehiro and Shigeo (JP 10-340,666) describe a field emission element. Kazunori and Shinsuke (JP 2001/111,217) provide a method of forming laminated wiring.

25

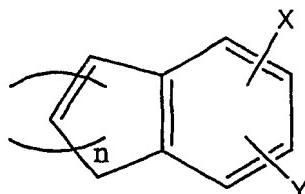
The present invention adds one or more UV-B blocking agents to a photoresist material from which a photo-imageable protective layer of an electronic device is made to reduce the formation of residue.

30

Summary of the Invention

One embodiment of the present invention is a composition comprising (a) a photoresist material, and 35 (b) a UV-B blocking agent selected from the group consisting of aromatic phenolic compounds and

carboxylic compounds that are described by the general formula:

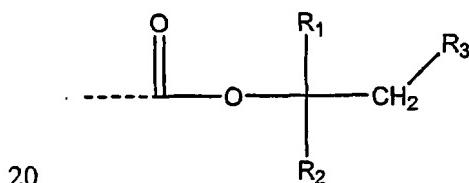


- 5 where n represent radicals of 1 or 2 carbon atoms or up to four additional conjugated benzene rings, and the aromatic and alkyl derivatives thereof, and X and Y may be either both hydroxy groups, both carboxyl groups, or one hydroxy and one carboxyl group.

10

- In a preferred embodiment, the photoresist material includes a polymer in which at least 50 mole percent of the monomers in the polymer comprise a structure selected from one or more members of the 15 groups consisting of:

(a)

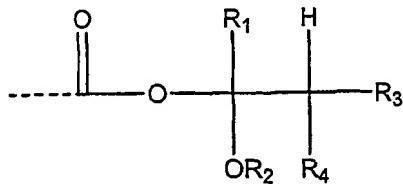


20

- wherein R₁ is hydrogen or lower alkyl; R₂ is a lower alkyl; and R₃ is hydrogen or a lower alkyl; and wherein a lower alkyl includes alkyl groups having 1 to 25 6 linear or cyclic carbon atoms;

30

(b)



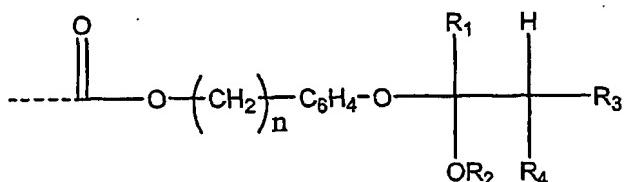
5

wherein R₁ is hydrogen or lower alkyl; R₂ is a lower alkyl; and R₃ and R₄ are independently hydrogen or a lower alkyl; and wherein a lower alkyl includes alkyl groups having 1 to 6 carbon atoms, and the joining of R₁ and R₂, or R₁ and either R₃ or R₄, or R₂ and either R₃ or R₄ to form a 5-, 6- or 7-membered ring; and

10

(c)

15



20

wherein R₁ is hydrogen or lower alkyl; R₂ is a lower alkyl; and R₃ and R₄ are independently hydrogen or a lower alkyl; and wherein a lower alkyl includes alkyl groups having 1 to 6 carbon atoms, and the joining of R₁ and R₂, or R₁ and either R₃ or R₄, or R₂ and either R₃ or R₄ to form a 5-, 6- or 7-membered ring.

25

In a further preferred embodiment, the phototresist material may also include 1 to 20 wt% of photoactive compounds.

30

In a further embodiment of the above composition, one or both of the hydroxy and carboxyl groups of the UV-B blocking agent are derivatized with

an ortho-nitro benzyl group, or with a t-butyl carboxyl group.

Another embodiment of the present invention
5 is a process to fabricate an electronic device in which
a composition as described above is deposited on a
substrate.

10 Brief Description of the Drawings

Figure 1 shows self-alignment of a UV-B blocking protective layer.

15 Detailed Description

The present invention provides a composition that can be used to make a photo-imageable protective layer in the fabrication of electronic devices. Protective layers are often patterned with an unfiltered light source, which could emit some amount of high energy UV-B radiation. Unfiltered light sources typically emit 365-465 nm radiation, and UV radiation of this frequency range is known as UV-A. For example, high-pressure mercury lamps emit particularly strong radiation at 356, 406 and 465 nm. UV-B is higher energy radiation in the range of 280 to 320 nm, and unfiltered high-pressure mercury lamps may emit small amounts of this radiation.

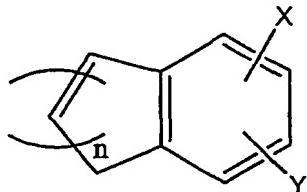
30 UV-B radiation can cause undesired photochemical reactions in a protective layer, resulting in formation of an insoluble residue. It is proposed herein to resolve the problem of such residue caused by UV-B radiation by formulating the protective
35 layer with a sufficient amount of UV-B blocking agent. Thus, the composition from which such protective layer is formed may contain about 0.001 to about 10 wt% of

UV-B absorbing agents in the formulation. The UV-B blocking agent can be admixed with essentially any photoresist material to form the composition from which the protective layer is formed. Frequently, novolac-type materials are used as a photoresist material.

Preferred UV-B blocking agents for use in this invention should meet several criteria. First, the blocking agents must absorb UV-B radiation, and it should be readily removed with the developing medium used for the photoresist material. It should also have sufficient thermal and photochemical stability to withstand the fabrication process. Excessive heat could make some compounds decompose or sublime from the protective layer.

Suitable UV blocking agents include aromatic compounds containing phenolic groups and/or carboxylic groups, with a general formula as follows

20



where n represent radicals of 1 or 2 carbon atoms or up to four additional conjugated benzene rings, and the aromatic and alkyl derivatives thereof, and X and Y may be either both hydroxy groups, both carboxyl groups, or one hydroxy group and one carboxyl group. The alkyl derivatives may include, for example, C₁-C₁₀ straight chain, branched or cyclic radicals, and the aromatic derivatives may include, for example, C₆-C₁₂ phenolic radicals with optional alkyl substituents.

The carboxyl or hydroxy groups can be protected with either photo-labile groups or acid-

labile groups to improve development contrast. For example, these groups can be derivatized with an ortho-nitro benzyl group, which can be deprotected with UV-A radiation. In another embodiment, however, these 5 groups can be protected with a t-butyl carboxyl group, which can be cleaved off by an acid catalyzed reaction with acid generated during the photolysis step for the photoresist. As the UV-B agent with these protecting groups is insoluble in the base developer, the loss 10 from the non-exposed area during the development would be minimized.

Migration of UV absorber molecules out of the matrix polymer in the photoresist material, 15 particularly surface blooming by thermal diffusion, is a potential drawback of these compounds, and it is influenced by the free volume of the polymer as well as by the size and shape of the diffusing molecules. Thus the UV blocking agent has to be selected to have good 20 compatibility with the polymer in the photoresist material of the protective layer, good solubility in the processing solvent, as well as high blocking efficiency.

25 The amount of UV blocking agent in the composition with the photoresist material may range between about 0.0001 to about 20 percent by weight of the total mixture. A more preferred range is about 0.01 to about 2 wt%. The amount of the blocking agent 30 required for the application depends on the types of UV light, the thickness of the protective layer and the absorption characteristics of the agent. Some of the agent could be sublimed during the heat treatment, and may undergo photolytic or thermal decomposition, so 35 that the efficacy of UV blocking could be process dependent. Too much blocking agent will make the photoresist less sensitive, and may require a large

amount of photo energy for photo development. The amount of photo blocking agent can be modulated to obtain a desirable balance between photo definition and photo blocking.

5

The amount of UV blocking agent can be adjusted depending on the degree of UV blocking required. The amount of additional radiation required to generate a residue-free pattern with the addition of 10 a corresponding amount of a UV blocking agent is a good indication how effectively the blocking agent blocks light. The absolute value can change depending on the thickness of film and radiation source. The efficacy of the UV blocking agent depends on the absorptivity 15 and energy dissipation mechanism as well as the presence of impurities.

A self-aligned environment in device fabrication is one in which one or more layers of the 20 device blocks radiation with the result that such a layer functions as a built-in photomask. The advantage of such a fabrication method is that the subsequent photo-patterning of other layers does not need to be conducted with a carefully aligned external photomask. 25 This enables shortening the fabrication time and the use of simpler equipment.

Although the photo-imageable protective layer can be used to enhance the contrast in a photo- 30 imageable thick film between the region that is directly irradiated and the region that is shielded by the protective layer, there is a potential problem related to the compatibility of the thick film paste with the protective layer. This problem may be 35 addressed by fabricating the protective layer from positive photo-imageable materials that do not degrade or dissolve upon contact with the high boiling ester-

type or ether-type solvents found in the thick film pastes, which solvents typically include butyl carbitol, butyl carbitol acetate, dibutyl carbitol, dibutyl phthalate, texanol and terpineol. The compatibility problem may be resolved by using, in the photoresist material of the protective layer, polymers with pendant acid labile groups. Upon either chemical treatment or photo-irradiation, such polymers become insoluble to ester-type organic solvents used with thick film pastes. A film of such polymers used as the protective layer is, however, highly transparent to high-pressure mercury lamp ultra violet radiation, which is typically used in photo fabrication. The mercury lamp radiation includes high intensity light at 365 nm (I-line) or 436 nm (g-line) radiation, or broad band unfiltered light including g-line and I-line radiation. The UV radiation in this wavelength range is frequently called UV-A.

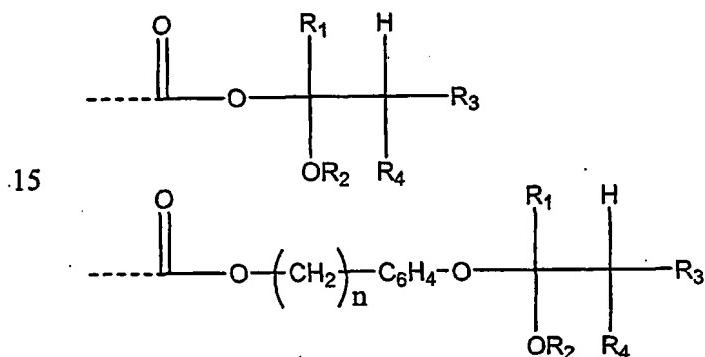
Self-alignment is most commonly achieved through back radiation. Figure 1 depicts self-alignment with an UV blocking protective layer. In Figure 1, the substrate (1) is a transparent support material, such as glass or polymer film. The protective layer (2) is coated on the top of the substrate material and then photo imaged to provide a pattern. A photosensitive thick film paste material (3) is applied on top of the photo-imaged protective layer. After evaporation of the solvent, UV radiation (5) is applied from the backside of the thick film paste, so that the photo irradiated area is hardened (4). In some instances, UV-B light in the radiation can cause residue-forming side reactions either by photochemically initiated oxidation reactions or by photochemical cyclization reactions. These side reactions can be reduced by the addition of UV-B

blocking agents to the composition from which the protective layer is prepared.

Novalac-type phenolic/formaldehyde polymeric materials are often used as the photoresist material in a protective layer in a process for the fabrication of an electronic device that contains a photo-imageable thick film paste such as Fodel® silver paste. The role of such a protective layer is to maintain spacing between the thick film deposit and other substrate structures to prevent contamination of the bottom substrate with the thick film paste. As mentioned above, in some cases, contamination of the bottom substrate may lead to short circuits. The protective layer is then removed by dissolution along with the unimaged thick film material. A drawback of these protective layers, however, is that they are frequently damaged during the process of applying the paste materials on the top of the protective layer. The cause of the damage is either the dissolution of the protective layer by solvent vapors generated during the paste drying process, or plastic deformation of the resist material due to plastization by these vapors. Butyl carbitol, butyl carbitol acetate, dibutyl carbitol, dibutyl phthalate, texanol and terpineol are examples of the solvents currently used in thick film paste formulation.

It may thus be desirable in this invention to use in the protective layer a photoresist material that shows either lower solubility or improved compatibility toward high boiling ester-type or ether-type solvent vapors so as to reduce the damage to the protective layer. A polymer to be used as the photoresist material from which a protective layer in electronic device is fabricated must be soluble in an organic solvent so that the polymer can be applied as a thin

film on the top of prefabricated device layers. Upon either chemical treatment or photo-irradiation, the polymer becomes impervious to ester-type or ether-type organic solvents used in the formulation of the thick film paste. Since the polymer must undergo a photo-imaging step to be used as the protective layer, it must also be formulated with a photo-responsive agent. A preferred polymer for this function contains a labile pendant group on a side acid functional group, which can be removed from the polymer pendant group at an appropriate time. One type of pendant acid labile group useful in the compositions of this invention may be described by the formulae:



wherein

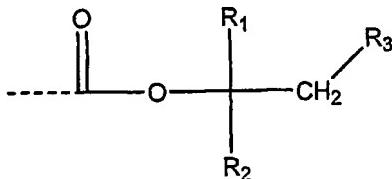
n = 0 to 4;
 20 R₁ is hydrogen or lower alkyl; R₂ is lower alkyl; and R₃ and R₄ independently are hydrogen or lower alkyl; and wherein a lower alkyl includes alkyl groups having 1 to 6 carbon atoms, and the joining of R₁ and R₂, or R₁ and either R₃ or R₄, or R₂ and either R₃ or R₄ to form a 5-, 6- or 7-membered ring.

Some examples of representative acid labile monomeric components, which may be used to prepare a polymeric photoresist material, include without limitation:

1-ethoxyethyl methacrylate (or acrylate),
 1-butoxyethyl methacrylate (or acrylate),
 1-ethoxy-1-propyl methacrylate (or acrylate),
 tetrahydropyranyl methacrylate (or acrylate),
 5 tetrahydropyranyl p-vinylbenzoate,
 1-ethoxy-1-propyl p-vinylbenzoate, 4-(2-
 tetrahydropyranyloxy)benzyl methacrylate (or acrylate),
 and
 10 4-(1-butoxyethoxy)benzyl methacrylate (or
 acrylate).

Another type of pendant acid labile group useful in the compositions of this invention may be described by the formulae:

15



wherein R₁ is hydrogen or lower alkyl; R₂ is lower alkyl; and R₃ is hydrogen or lower alkyl; and
 20 wherein a lower alkyl includes alkyl groups having 1 to 6 linear or cyclic carbon atoms

Other examples of representative acid labile monomeric components, which may be used to prepare a
 25 polymeric photoresist material, include without limitation::

t-butyl methacrylate (or acrylate),
 neopentyl methacrylate (or acrylate),
 1-bicyclo{2,2,2}octyl methacrylate (or acrylate)
 30 and their derivatives,
 1-bicyclo{2,2,1}heptyl methacrylate (or acrylate)
 and their derivatives,
 1-bicyclo{2,1,1}hexyl methacrylate (or acrylate)
 and their derivatives,

1-bicyclo{1,1,1}pentyl methacrylate (or acrylate) and their derivatives, and

1-adamantyl methacrylate (or acrylate) and their derivatives.

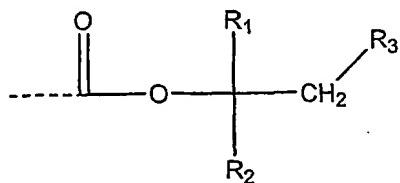
5

The preferred molecular weight of the polymer in a photoresist material is 7,000-1,000,000. It is also desirable to use copolymers, either random or block copolymers, of monomer units containing acid 10 labile side groups as well as other monomers that do not have acid labile pendant groups but have hydrophilic groups such as ethylene glycol ethers or carboxylic acid groups. Molecular weights higher than conventional photoresist materials are preferred since 15 the polymer film deposited as the protective layer has to withstand various mechanical processes, such as screen printing. Mechanical stress is applied to the film with a rubber squeeze during or after the screen printing. In order to improve organic solvent 20 resistance, it would be desirable to have a high amount of acid after the removal of the labile groups. The amount of monomer in the copolymer suitable for impermeability to the organic vapor depends on the types of organic solvent used with the paste. The 25 preferred mole fraction for the monomer containing a labile ester group is at least about 50 mol%, and the more preferred mole percentage is at least about 60 mol%.

30

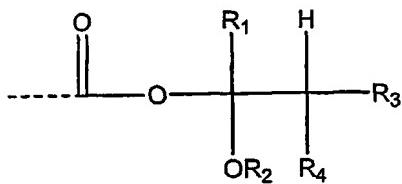
The present invention is thus particularly useful when the photoresist material in the composition is prepared from polymers in which at least 50 mole percent of the monomers in the polymer include a structure selected from one or more members of the 35 groups consisting of:

(a)



- 5 where R₁ is hydrogen or lower alkyl; R₂ is a lower alkyl; and R₃ is hydrogen or a lower alkyl; and wherein a lower alkyl includes alkyl groups having 1 to 6 linear or cyclic carbon atoms;

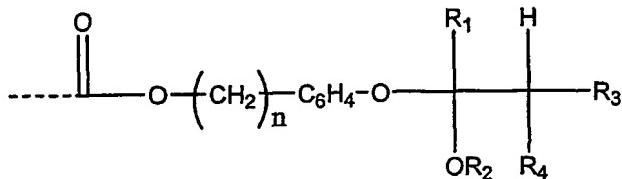
10 (b)



- 15 wherein R₁ is hydrogen or lower alkyl; R₂ is a lower alkyl; and R₃ and R₄ are independently hydrogen or a lower alkyl; and wherein a lower alkyl includes alkyl groups having 1 to 6 carbon atoms, and the joining of R₁ and R₂, or R₁ and either R₃ or R₄, or R₂ and either R₃ or R₄ to form a 5-, 6- or 7-membered ring; and

20

(c)



- 25 wherein R₁ is hydrogen or lower alkyl; R₂ is a lower alkyl; and R₃ and R₄ are independently hydrogen or a lower alkyl; and wherein a lower alkyl includes alkyl groups having 1 to 6 carbon atoms, and the joining of

R₁ and R₂, or R₁ and either R₃ or R₄, or R₂ and either R₃ or R₄ to form a 5-, 6- or 7-membered ring.

- Suitable polymers on which to base a
5 photoresist material may include those prepared from monomers in the group consisting of 1-ethoxyethyl methacrylate, 1-ethoxyethyl acrylate, 1-butoxyethyl methacrylate, 1-butoxyethyl acrylate, 1-ethoxy-1-propyl methacrylate, 1-ethoxy-1-propyl acrylate,
10 tetrahydropyranyl methacrylate, tetrahydropyranyl acrylate, tetrahydropyranyl p-vinylbenzoate, 1-ethoxy-1-propyl p-vinylbenzoate, 4-(2-tetrahydropyranyloxy) benzyl methacrylate, 4-(2-tetrahydropyranyloxy) benzyl acrylate, 4-(1-butoxyethoxy) benzyl methacrylate, , 4-
15 (1-butoxyethoxy)benzyl acrylate t-butyl methacrylate, t-butyl acrylate, neopentyl methacrylate, neopentyl acrylate, 1-Bicyclo{2,2,2}octyl methacrylate (or acrylate) and their derivatives, 1-Bicyclo{2,2,1}heptyl methacrylate (or acrylate) and their derivatives, 1-
20 Bicyclo{2,1,1}hexyl methacrylate (or acrylate) and their derivatives, 1-Bicyclo{1,1,1}pentyl methacrylate (or acrylate) and their derivatives and 1-adamantyl methacrylate (or acrylate) and their derivatives.

25 Block copolymers can be prepared by methods known in the art, using methods typically known as living or controlled polymerization, like anionic or group transfer polymerization as well as atom transfer polymerization. Techniques regarding living,
30 controlled and atom transfer polymerization suitable for use herein include those described in "Controlled/Living Radical Polymerization", edited by K. Matyjaszewski, Oxford University Press. Random copolymers can be obtained by solution polymerization
35 using typical free radical initiators, such as organic peroxide and azo initiators. Methods for random copolymer polymerization suitable for use herein

include those described in "Polymer Chemistry", Fifth Edition by C.E. Carraher, Jr., Marcel Dekker Inc., New York, New York. (Chapters 7, 8 and 9); or "Polymers" by S.L. Rosen in The Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, John Wiley and Sons Inc., New York (Volume 19, pages 899-901).

A photo-initiator when used is selected from conventional photo acid generators such as aromatic sulfonium phosphofluoride, antimony fluoride, or aromatic iodonium salt with similar anions. Suitable photo acid generators for use herein include those described in a paper by J.V. Crivello, "The Chemistry of Photoacid Generating Compounds" in Polymeric Materials Science and Engineering, Vol. 61, American Chemical Society Meeting, Miami FL, Sept. 11-15, 1989, pages 62-66 and references therein. The selected photo acid generator should not undergo decomposition or dissolution during the development stage.

Representative examples of nonionic photoacid generators include PI-105 (Midori Kagaku Co, Tokyo, Japan), a high molecular weight photo acid generator such as CyraCure UVI 6976 (Dow Chemical, Midland MI), or CD-1012 (Aldrich Chemical, Milwaukee WI).

Suitable UV-B blocking agents include compounds that absorb UV light in the range of 250 to 320 nm. These agents should have low solubility in aqueous base developing solutions while they are mixed with a photoresist material to form the composition from which the protective layer is formed. The UV-B blocking agent should become readily soluble in the developing solution as photochemically induced deprotection of the acid labile ester group of the matrix polymer in the photoresist material renders the matrix polymer soluble in the developing solvent. Such

compounds are exemplified by aromatic compounds containing phenolic groups and/or carboxylic groups.

The UV blocking agent is selected to have compatibility with all these additives, and should be soluble in the solvent. In addition, it should not decompose or be washed out during the radiation and development stages. The preferred UV blocking agents are 2,3 dihydroxy and 1-5- dihydroxy naphthalene, and 10 their o-nitro benzyl or t-butyl carbonate derivatives.

The present invention further provides a process of fabricating an electronic device by depositing a composition of this invention on a substrate. The substrate may be a component in an electronic device structure along with a positive photo-imageable protective layer, which is prepared from a composition of a photoresist material and a UV-B blocking agent, and layer of thick film paste. When 20 the substrate has a conducting layer deposited on it, the substrate may be an electronic device itself.

To fabricate an electronic device using the process of this invention, a 0.5 to 40 micron thick coating of a composition of a polymeric photoresist material with pendant labile acid groups, photo-active reagents and one or more UV blocking agents is applied to a substrate as a protective layer. Such coating could be achieved by spin coating or table coating 30 using a blade in an appropriate organic solvent. The preferred organic solvents for applying the coating are propylene glycol 1-monomethyl ether 2-acetate (PGMEA) or cyclohexanone.

35 Next, the solvent is removed by heating the substrate to between about 70 to 100°C for typically about 1 to 3 minutes on a hot plate. The coating is

then ready to be patterned by UV photo-irradiation through a mask. UV irradiation followed by heat treatment will cleave acid labile pendant groups to convert the ester to the acid. The UV photo 5 irradiation source may be a mercury lamp. For a higher wavelength than 248 nm, it may be desirable to add a small amount (10-10000 ppm) of photosensitizer, which will increase the absorption of UV light. Representative examples of suitable photosensitizers 10 include isopropylthioxanthone (ITX), 2,4-Diethyl-9H-thioxanthen-9-one (DETX) and benzophenone. The UV irradiation dose is 50 to 3000 mJ/cm².

Post exposure baking conditions are typically 15 about 120 to 140°C for about 1 to 3 minutes. This treatment causes the exposed area to be soluble in an aqueous base developing solvent. The basic developing solvents may include a carbonate solution or a low concentration sodium or potassium hydroxide solution. 20 Preferably, a commercial aqueous base developer, such as AZ 300, 400 or 500, obtained from Clariant Corporation (AZ Electronic Materials, Somerville NJ), can be used.

25 After development, the protective layer serves as a patterned template. The remaining portions of the protective layer are still soluble in organic solvents, however, and the protective function thereof toward the thick film paste is thus limited. The layer 30 can be converted to a high polycarboxylic acid content, which is insoluble in the common organic solvents employed in thick film pastes, by exposure to UV light and subsequent heat treatment. The UV irradiation dose is typically about 50 to 4000 mJ/cm². Post exposure 35 baking conditions are typically about 120 to 140°C for 1 to 3 minutes.

A suitable thick film paste for use in an electronic device, as made by the process described above, is a paste that is negatively-imageable and may be developed with an aqueous base. A representative example is Fodel® silver paste. The pastes may also contain carbon nanotubes for field emission display applications. Thick film paste is applied on the top of the converted protective layer by such methods as screen printing, which fills the vacancies in the patterned template generated by photo development. Subsequently, the thick film paste is photo irradiated from the back side of the structure. The paste located in the patterned template where the protective layer is removed by photo-imaging would be imaged preferentially. As the paste is negatively developed upon irradiation, it becomes insoluble to developing solvents. Typically, these thick film pastes are developed by gentle spray of an aqueous base solution. The unimaged paste is washed out within a length of time that is referred to as the time-to-clear (TTC). Typically, the spray will last about 1.5 to about 3.0 times the TTC. As the irradiated protective layer is soluble in the aqueous base solution, it is removed while the unimaged thick film paste is being removed as it is spray developed.

The advantageous effects of this invention are demonstrated by a series of examples, as described below. The embodiments of the invention on which the examples are based are illustrative only, and do not limit the scope of the appended claims.

Example 1

The following components are mixed with 5.97 g of PGMEA to give a clear solution:

- 5 3.270 grams of poly(ethoxytriethylene glycol methacrylate-*b*-*t*-butyl methacrylate) having a degree of polymerization (D.P.) of 37/100, and a number average molecular weight (Mn) of 10,000,
- 10 0.70 grams CyraCure® UVI-6976 photo acid generator solution (Dow Chemical, Midland MI),
- 15 0.17 grams of a 1% Quanticure ITX solution photosensitizer in PGMEA (Aldrich),
- 20 0.68 g of a 1% 2,3-diazabicyclo[3.2.2]non-2-ene,1,4,4-trimethyl-,2,3-dioxide (TAOBN) solution in PGMEA, and
- 25 0.04 g of a 1% 2,3 dihydroxy naphthalene solution in methyl ethyl ketone.

Using a 2 mil doctor blade, the solution is cast on an indium tin oxide-coated glass plate and allowed to air dry for 10 minutes. The film is then dried for 2 min at 70°C on a hot plate. The film is exposed to a 2000 mJ/cm² broad band UV light using a 20 micron photomask, and then heat treated on a hot plate at 120°C for 2 minutes. The imaged part is developed by spraying with a 0.5% sodium carbonate solution containing 3% surfactant. A clean image is observed. The plate is rinsed with deionized water, and dried on a 90°C hot plate, then flood exposed with a 200 mJ/cm² light. The plate is then baked at 120°C for 2 minutes, and then developed with the same developer. Complete removal of the polymer is observed.

Example 2

- 35 1,5-dihydroxy naphtalene is used instead of 2,3-dihydroxy naphtalene in the same manner as described in Example 1. A similar result is observed.

Example 3

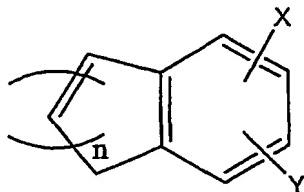
2-naphthol is used instead of 1,5-dihydroxy naphthalene in the same manner as described in Example 5 2. Some residue is observed in the pattern.

CLAIMS

What is claimed is:

- 5 1. A composition comprising (a) a photoresist material, and (b) a UV-B blocking agent selected from the group consisting of aromatic compounds containing phenolic groups and/or carboxylic groups described by the general formula:

10



wherein n represents radicals of 1 or 2 carbon atoms or up to four additional conjugated benzene rings, and the aromatic and alkyl derivatives thereof; and X and Y
15 may either be both hydroxy groups, both carboxyl groups, or one hydroxy group and one carboxyl group.

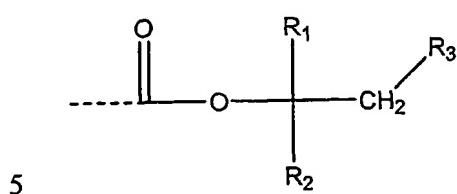
2. The composition of Claim 1 wherein one or both of the hydroxy and carboxyl groups of the UV-B
20 blocking agent are derivatized with an ortho-nitro benzyl group, or with a t-butyl carboxyl group.

3. The composition of Claim 1 further comprising (c) 1 to 20 wt% of photoactive compounds.

25

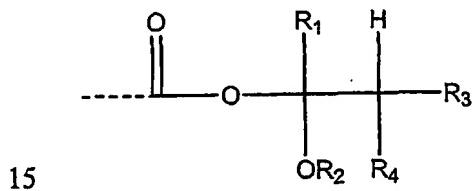
4. The composition of Claim 1 wherein the photoresist material comprises a polymer in which at least 50 mole percent of the monomers comprise a structure selected from one or more members of the
30 groups consisting of:

(a)



wherein R₁ is hydrogen or lower alkyl; R₂ is lower alkyl; and R₃ is hydrogen or lower alkyl; and wherein a lower alkyl includes alkyl groups having 1 to 6
10 linear or cyclic carbon atoms;

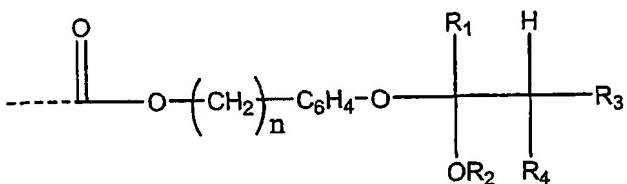
(b)



wherein R₁ is hydrogen or lower alkyl; R₂ is lower alkyl; and R₃ and R₄ are independently hydrogen or lower alkyl; and wherein a lower alkyl includes alkyl groups having 1 to 6 carbon atoms, and the joining of R₁ and R₂, or R₁ and either R₃ or R₄, or R₂ and either R₃ or R₄ to form a 5-, 6- or 7-membered ring; and
20

(c)

5



wherein R₁ is hydrogen or lower alkyl; R₂ is lower alkyl; and R₃ and R₄ are independently hydrogen or lower alkyl; and wherein a lower alkyl includes alkyl groups having 1 to 6 carbon atoms, and the joining of R₁ and R₂, or R₁ and either R₃ or R₄, or R₂ and either R₃ or R₄ to form a 5-, 6- or 7-membered ring.

15 5. The composition of Claim 4 wherein the monomer is selected from one or more members of the group consisting of 1-ethoxyethyl methacrylate, 1-ethoxyethyl acrylate, 1-butoxyethyl methacrylate, 1-butoxyethyl acrylate, 1-ethoxy-1-propyl methacrylate, 20 1-ethoxy-1-propyl acrylate, tetrahydropyranyl methacrylate, tetrahydropyranyl acrylate, tetrahydropyranyl p-vinylbenzoate, 1-ethoxy-1-propyl p-vinylbenzoate, 4-(2-tetrahydropyranyloxy) benzyl methacrylate, 25 4-(2-tetrahydropyranyloxy) benzyl acrylate, 4-(1-butoxyethoxy) benzyl methacrylate, 4-(1-butoxyethoxy)benzyl acrylate, t-butyl methacrylate, t-butyl acrylate, neopentyl methacrylate, neopentyl acrylate, 1-Bicyclo{2,2,2}octyl methacrylate 30 (or acrylate) and their derivatives,

1-Bicyclo{2,2,1}heptyl methacrylate (or acrylate) and their derivatives, 1-Bicyclo{2,1,1}hexyl methacrylate (or acrylate) and their derivatives,
1-Bicyclo{1,1,1}pentyl methacrylate (or acrylate) and
5 their derivatives, and 1-adamantyl methacrylate (or acrylate) and their derivatives.

6. A process of fabricating an electronic device comprising depositing the composition of any one
10 of Claims 1, 2, 3, 4 or 5 on a substrate.

7. The process of Claim 6 wherein the substrate is an electronic device.

15 8. The process of Claim 6 wherein the electronic device comprises a thick film paste.

9. The process of Claim 8 wherein the thick film paste comprises carbon nanotubes.

20

Figure 1

